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(54) Process for self-hydrogenation

(57) A process for the
self-hydrogenation of the olefins,
present in refinery gases, at levels of
6-15% by volume or higher, whereby,
after separating liquid from the refinery
gases stream, a portion of said stream
which makes up the feed of the
ammonia unit, is admixed to saturated
cooled recycle gas and compressed
under controlled pressure and the
mixture feed-recycle gas is
hydrogenated in the fixed bed
hydrogenation reactor, so as to reduce
the olefin levels to less than 0,3% by
weight, and at the same time COS is
hydrogenated into H_2S, a portion of the
hydrogenated gas is carried to a zinc
oxide reactor in order to remove H_2S, the
olefin-free and sulphur-free gas is
injected in the steam reformer, another
portion of the hydrogenated gas from
the hydrogenation reactor is returned to
a heat exchanger in order to give heat to
the feed, said gas is cooled in another
exchanger and the hydrogenated gas is
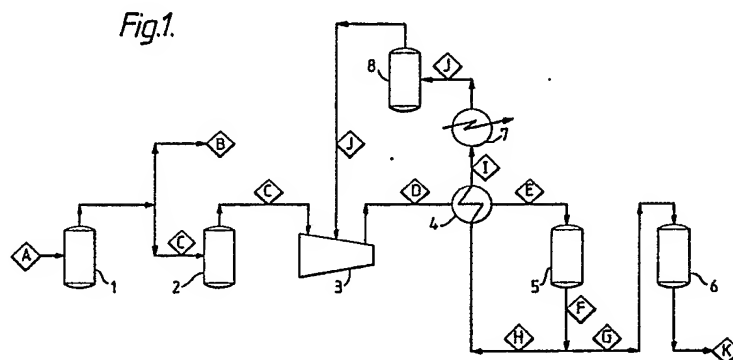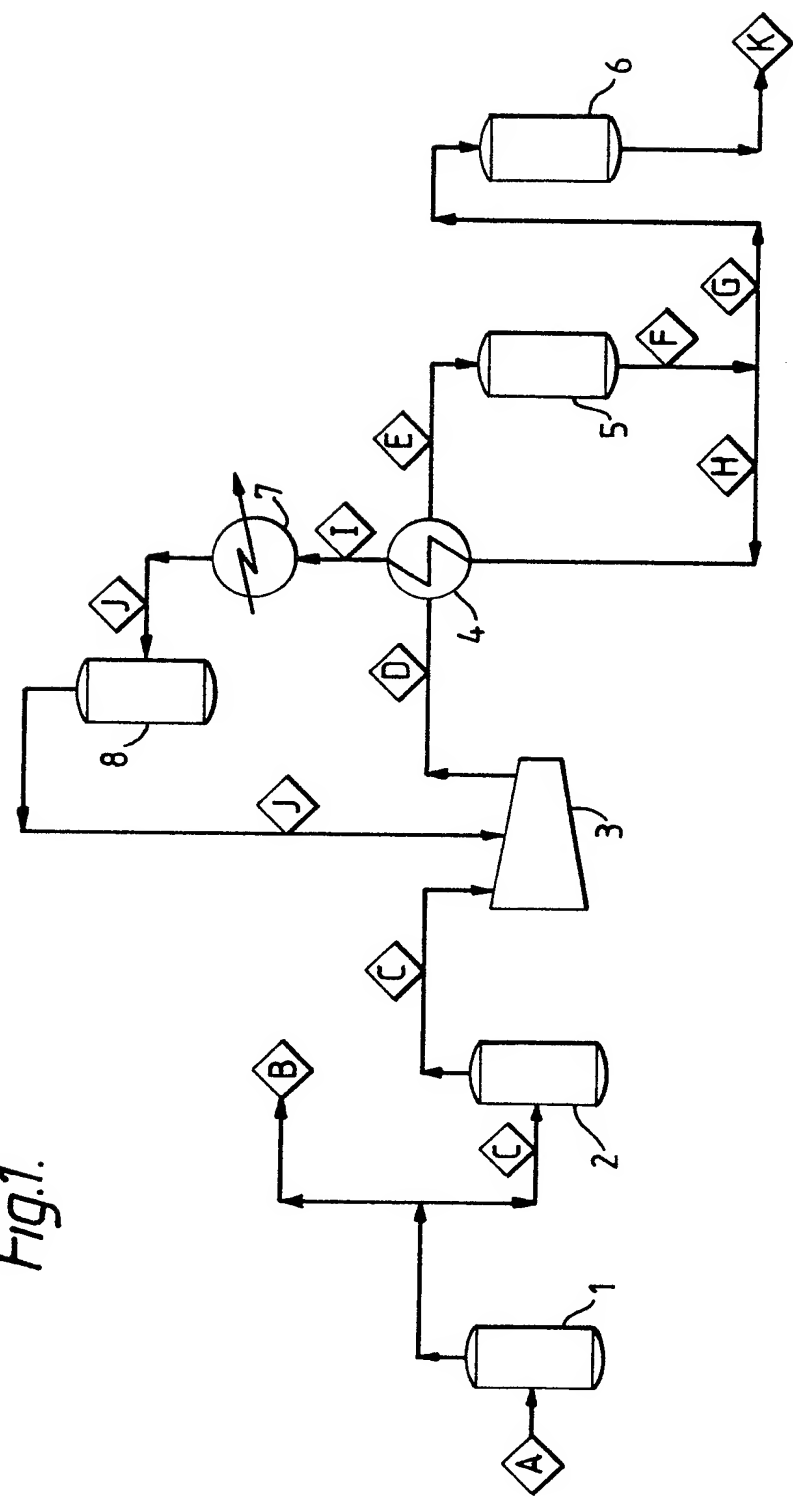injected in the compressor intermediate
stage.

Fig.1.

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Fig1.

SPECIFICATION

Process for self-hydrogenation

5   This invention relates to a process for the self-hydrogenation of the olefins present in the refinery gases.   5
      More specifically, the present invention relates to a process for the self-hydrogenation of the olefins
    present in the refinery gases which can then be steam-reformed in order to produce hydrogen. The thus
    obtained hydrogen can, for example, be admixed to air nitrogen under pressure, making up the synthesis
    gas of ammonia. It can equally well be directed to the production of other petrochemicals or else to the
10 treatment of petroleum fractions.   10
      Ammonia is one of the most important chemicals, and its use as a fertilizer or as an intermediate in the
    preraration of other fertilizers as urea, ammonium nitrate, ammonium sulfate is intensive, and its
    consumption is ever increasing.
      The synthesis of ammonia from its elements, hidrogen and nitrogen, has been developed since 1913,
15 passing through the preparation of synthesis gas, made up chiefly of hydrogen and nitrogen, whose reaction 15
    produces ammonia. While the source of nitrogen for this reaction has always been air, the hydrogen source
    has varied, according to the availability of raw materials and economic considerations.
      Thus, coal and coke have already been employed as raw material for the production of hydrogen. For
    example, the Winkler process used to crack coal in a fluidized bed using nearly pure oxygen, thus permitting
20 the recovery of several hydrocarbons as by-products. More recently, the availability of natural gas and of   20
    petroleum fractions has allowed new developments in the production of synthesis gas:
    — non-catalytic partial oxidation;
    — methane or naphtha steam-reforming.
      The first process is interesting due to the fact that it accepts feeds of different hydrocarbon compositions,
25 from natural gas up to heavy fuel oil, but is requires the additional building of an air plant.   25
      Presently the more used process is the methane reforming with steam, under the action of catalysts. This
    process is conducted in two catalytic reactional stages. In the first stage of primary reforming, one obtains a
    partially reformed gas, which contains approximately 10% by volume of methane (dry basis) and in the
    secondary reformer this gas is processed up to the low methane level required for the synthesis gas
30 production, which must not exceed 0,3 to 1,0% by volume.   30
      The process conditions for the reaction of steam on natural gas produce CH_4, H_2O, CO, CO_2 and H_2. An
    important condition is that there not be formation of carbon on the catalyst, causing loss of its activity.
    Furthermore, the reforming catalyst is reactive to the presence of sulphur in the hydrocarbon feed, that is
    why the feed generally suffers a desulphurization process before the steam reforming.
35   The basic reaction of reforming can be represented by   35

$$CH_4 + H_2O \rightarrow CO + 3\ H_2$$

    This reaction is strongly exothermic and is thus favored by elevated temperatures and a high steam level.
40 Typically, at the exit of the primary reformer the temperature reaches 821 °C (1510 °F) and 33,4 kg/cm^2 (475 40
    psia), while the effluent from the secondary reformer will have a temperature of 999°C (1830°F).
      The gas produced in the reforming reactor contains three forms of carbon: methane, CO and CO_2. The
    following step consists in submitting carbon monoxide to the shift reaction, whereby CO, by reaction with
    steam under the action of an iron-based catalyst produces CO_2 and H_2, whith heat evolution:
45   45

$$CO + H_2O \rightarrow CO_2 + H_2$$

    Carbon dioxide is removed by contacting with monoethanolamine solution at 30% (MEA) or hot carbonate,
    and the residual CO level is around 0,5%, dry basis. It is further necessary before the step of the ammonia
50 synthesis, to convert into methane the small remaining amounts of CO and CO_2 due to their oxidizing effects 50
    on the catalyst employed in the synthesis of ammonia, which is generally nickel. The methanation reaction
    lowers these oxides levels to less than 10 ppm. These exothermic reactions can be represented by the
    equations:

55        $CO + 3\ H_2 \rightarrow CH_4 + H_2O$ 55
          $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$

    As the production of ammonia from its elements is a well-known process, the technical literature is abundant
    in information on the various aspects concerning the hydrogen production, for example, concerning the
60 source of this substance (coal, heavy residual oils, noble hydrocarbons such as naphtha, etc.), the catalysts 60
    employed in the reforming process, the purification processes, for example, desulphurization of gases to be
    submitted to steam reforming, etc.
      Under another aspect, the concern to producing hydrogen for synthesis gas or ammonia from cheaper
    hydrocarbon sources than noble petroleum fractions is quite old. Thus, US patent no. 1.864.717 preaches the
65 use of refineries waste products or of by-products for the preparation of ammonia. According to this patent,   65

if air is blowed through heavy oil heated to 400–500°C, the oxidation reaction gives various products and nitrogen (present in air) is incorporated into the reaction products. The mixture hydrogen-nitrogen is converted into ammonia.

GB patent no. 1.429.331 refers to the possibility of producing hydrogen-rich gas aiming at preparing
5 synthetic natural gas through the coupling of one fluid catalytic cracking plant where heavy hydrocarbons are cracked; the cracked product (naphtha) which contains olefins passes through a hydrogenation unit in order to saturate olefins and aromatics and to produce a saturated naphtha fraction which reacts with steam in a reforming unit to produce synthesis gas. Nevertheless, explicit details are lacking which could elucidate inequivocally a refinery gases hydrogenation.

10 In Brazil, due to the petroleum crisis, the preparation of hydrogen through the reforming of natural gas or naphtha is beginning to cause problems due to the scarcity of natural gas in this country and the high cost of naphtha. Another hydrocarbon source for the reforming process could be the refinery gas. A typical composition of this gas is listed on Table 1.

15   TABLE 1   15

Components	% vol
Hydrogen	21,81
20 Saturated compounds	56,78
Olefins	12,72
Nitrogen	5,96
Carbon monoxide	1,87
Carbon dioxide	0,01
25 Sulfides (COS+H_2S)	0,02
Water	0,83
Total	100,00

30 As can be seen from Table 1 above, the refinery gas presents, in its composition, unsaturated hydrocarbons (nearly 13%), which makes it not adequate for steam-reforming. The olefins cause large coke deposition on the reforming catalyst and their maximum allowed concentration in the feed is around 1% by weight.

The observation of Table 1 leads to the conclusion that, due to the fact that the hydrogen concentration in
35 the refinery gas is higher than the stoichiometric concentration necessary to saturate the olefins present in that gas, a catalytic self-hydrogenation process is made possible, according to the action:

$$C_nH_{2n}+H_2 \rightarrow C_nH_{2n+2}$$
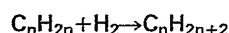
40 which reaction is quite exothermic.

Thus, although the refinery gas, by itself, is not adequate for the steam-reforming due to the presence of a relatively high level of olefins – around 13% by volume – its high hydrogen level – nearly 22% by volume – allows the use of the hydrogen itself contained in the refinery gas to saturate the olefins and thus to obtain a product which is adequate for the forming reaction of the synthesis gas.

45 A drawback in this process could be the trend to a heavy coke formation on the hydrogenation catalyst, which rapidly would turn the catalyst inactive. Actually, GB patent no. 1.430.121 refers to this problem and presents another route to make viable the steam-reforming, of a gas containing around 15% of olefins, whereby is employed steam-reforming catalyst containing silver in its composition.

Another problem with hydrogenation of refinery gases consists in the possibility of methanation reactions
50 to occur on the carbon oxides generally present in these streams. These reactions evolve a huge amount of heat which contributes to the temperature elevation, which can reach not acceptable levels.

Besides, the refinery gas, a mixture of gases from the fluid catalytic cracking, delayed coking and catalytic reforming plants, generally effluent from a treatment unit with diethanolamine (DEA), can contain around 100 ppm by volume of sulphydric gas besides highly variable concentrations of carbonyl sulfide (COS),
55 which requires additional treatment for the removal of sulphur to the level allowed in the reforming process (around 0,5 ppm by weight).

Under another point of view, it is of vital interest the knowledge of certain secondary reactions occurring in the presence of hydrogenation catalysts, in order to select an economical process of sulphur removal.

From the study of the drawbacks related above, the applicant has developed, on the basis of experiments
60 in pilot plant, which are now described, an economic process of catalytic hydrogenation of the refinery gas which makes it adequate for steam-reforming, allowing to employ conventional catalysts in the reforming.

Thus, for any hydrogen generation unit near a refinery, the present process provides an alternative to the substitution of natural gas or naphtha employed up to now as raw material for steam reforming. In effect, the applicant has made the scaling up of his hydrogenation pilot plant, making the project of a refinery gas
65 hydrogenation industrial plant which is operating 8 km from a refinery and which feeds an ammonia

production unit of 454 tons/day and whose feed was previously naphtha, the savings being of the order of US$ 9 million a year, besides the additional savings by the reduction in the raw material consumption and fuel, demonstrated in the operation.

Therefore, one object of the present intention is to provide a refinery gases catalytic hydrogenation
5   process which can be employed for steam reforming in the production of synthesis gas.   5

Another object of the present invention is to provide a refinery gas hydrogenation process such that the gases after hydrogenation can be treated for the removal of sulphur and immediately be submitted to a steam reforming process without excessive deposition of coke on the catalyst, which keeps excellent activity.
10   A simplified flowsheet of the process of the present invention is illustrated in *Figure 1*.   10

The hydrogenation process of the present invention which makes possible that refinery gas made up of gas produced in fluid catalytic cracking units (FCC) and delayed coking, alone or in admixture, containing between 6 and 15% by volume of olefins be the source of hydrocarbons which will supply the hydrogen for the ammonia synthesis is characterized by the fact that it comprises the following steps:
15   a) separating the liquid stream from a refinery gas stream A in a liquid separating vessel 1, the liquid-free   15
gas stream being split into two streams: a stream B feeding the fuel gas system and another stream C making up the ammonia plant feed;

b) passing stream C from step a) through a compressor suction drum 2 said stream being compressed, under pressure control, in compressor 3, causing the intermediate suction of the saturated and cooled gas
20   recycle and admixing of said gas with the feed and removing a portion of the reaction-generated heat from   20
the hydrogenation reactor 5;

c) compressing the mixture feed-recycle gas from step b) in compressor 3 under pressures in the range from 100–713 psi (7 to 50 kg/cm^2), or higher, preferably, 385–713 psi (27–50 kg/cm^2), thus forming stream D, said compressor 3 being able to receive low density gases with high concentration of hydrogen from the
25   cracking of heavy gasoil and from the vacuum residue with high levels of nickel;   25

d) heating stream D from step c) in exchanger 4, recovering heat from the recycle, effluent from hydrogenation reactor 5, passing mixture E feed-recycle gas through hydrogenation reactor 5, the ratio feed-recycle gas being controlled so that the temperature of said reactor 5 is kept at minimum levels of coke deposits on the catalyst without reduction of the rate of the hydrogenation reaction, the hydrogenation
30   reactor 5 being filled with a fixed bed catalyst made up of cobalt-molybdenum oxide, or nickel molybdenum,   30
said reactor being designed so that the space velocity obtained by the passage of gases is such that the hydrogenated product, stream F, is practically olefin-free, or that said product contains at the end of the campaign less than 0,3% by weight of olefins, the life-time of the campaign of the active catalyst reaching twelve or more months, and at the same time sulphur compounds such as carbonyl sulfide (COS), being
35   hydrogenated into sulphydric acid, said acid being further removed on a zinc oxide bed;   35

e) passing a portion of the hydrogenated gas, stream G, effluent from hydrogenation reactor 5 from step d) through a zinc oxide fixed bed reactor 6 in order to remove as zinc sulfide the sulphydric acid existing in the refinery gas or produced in step d) followed by injection of the hydrogenated and sulphur-free refinery gas – stream K – in the steam reformer;
40   f) returning a portion of the hydrogenated gas – stream H – effluent from the hydrogenation reactor 5 to   40
the heat exchanger 4 in order to cool said gas and give heat to the feed, followed by cooling said gas – stream I – in the exchanger 7 with water, optionally boiler water up to temperatures in the range of 170–140°C, preferably 150°C, separating in vessel 8 the liquid formed, followed by injection of said gas – stream J – in the intermediate stage of the compressor 3.
45   Notice that in the reaction step occurring in the hydrogenation reactor 5, the set of variables, pressure,   45
temperature and space velocity is such that, methanation reactions of the carbon oxides present in the refinery gases, highly exothermic, are kept under control. Thus, pressure is kept between 100 to 713 psi (7–50 kg/cm^2), preferably 543 psi (38 kg/cm^2), the temperature between 250 and 400°C, preferably 360°C and the hourly space velocity between 700 and 2500 h^{-1}, preferably 1250 h^{-1}. It is also obtained the hydrogenation of
50   sulphur compounds such as carbonyl sulfide (COS), usually present in gases from fluid catalytic cracking   50
units (FCC), which forms sulphydric acid, which allows its further removal in a zinc oxide bed.

Another occurring reaction is the shift of carbon monoxide present in the refinery gases, going to carbon dioxide through the reaction with the equilibrium water present in the refinery gases. The amount of formed CO$_2$ is such that could make non economic a caustic process for sulfphur removal.
55   Still in the reaction step, due to the huge variations in composition which can occur int the refinery gases,   55
chiefly concerning the olefin level, an adequate instrumentation of the reactor is included in the said process such as to avoid exceeding, at any moment, at any point of the bed, the temperature in which there is great acceleration of the coke deposition reactions on the catalyst. Notice that in spite of the low coke deposition on the catalyst, it is advisable to have a spare reactor of identical dimensions to the principal reactor and
60   connected in parallel to said chief reactor, so that is guaranteed the operational continuity of the ammonia   60
unit, during the CoMo or NiMo catalyst regeneration procedure, conducted of conventional manner by roasting, passing air on the deposited carbon.

The present process is still characterized in that all the heat necessary to the hydrogenation reactions is obtained from those reactions and that all the required hydrogen is originally found in the refinery gas itself,
65   thus, the need for additional injection of hydrogen not existing.   65

The now presented process, on the opposite to what say some literature sources, concerning the difficulty to controlling the coke deposition on the catalyst, keeps under control the rate of the coke deposition reactions on the catalyst.   •

Finally, this is an industrial process whose efficiency and economicity are already demonstrated in a pilot

5 plant which has been the subject of a scaling up to a production industrial plant for ammonia of 454 ton/day,   5
and which is in operation. This unit allows savings in foreign currency of the order of US$ 9 million/year,
from the substitution of refinery gas for naphtha, with return of the capital investment of less than one year.

Among other advantageous aspects of the substitution of refinery gases for naphtha, the present process
is presenting, in the industrial unit, global savings in raw material and fuel of the order of 10% as compared

10 to the operation with naphtha.   10

CLAIMS

1.   A PROCESS FOR THE SELF-HYDROGENATION of refinery gases from fluid catalytic cracking plants

15 (FCC) and from delayed coking plants, said gases containing from 6 to 15% olefins by volume, *characterized*   15
by:
   a)   separating the liquid stream from a refinery gas stream A in a liquid separating vessel 1, the liquid-free
gas stream being split into two streams: a stream B feeding the fuel gas system and another stream C
making up the ammonia plant feed;

20   b)   passing stream C from step a) through a compressor suction drum 2 said stream being compressed,   20
under pressure control, in compressor 3, causing the intermediate suction of the saturated and cooled gas
recycle and admixing of said gas with the feed and removing a portion of the reaction-generated heat from
the hydrogenation reactor 5;
   c)   compressing the mixture feed-recycle gas from step b) in compressor 3 under pressures in the range

25 from 100–713 psi (7 to 50 kg/cm^2) or higher, preferably, 385–713 psi (27–50 kg/cm^2), thus forming stream D,   25
said compressor 3 being able to receive low density gases with high concentration of hydrogen from the
chacking of heavy gasoil and from the vacuum residue with high levels of nickel;
   d)   heating stream D from step c) in the exchanger 4, recovering heat from the recycle, effluent from the
hydrogenation reactor 5, passing mixture E feed-recycle gas through hydrogenation reactor 5, the ratio

30 feed-recycle gas being controlled so that the temperature of said reactor 5 is kept at minimum levels of coke   30
deposits on the catalyst without reduction of the rate of the hydrogenation reaction, the hydrogenation
reactor 5 being filled with a fixed bed catalyst made up of cobalt-molybdenum oxide, or nickel-molybdenum,
said reactor being designed so that the space velocity obtained by the passage of gases is such that the
hydrogenated product, stream F, is practically olefin-free, or that said product contains at the end of the

35 compaign less than 0.3% by weight of olefins, the life-time of the campaign of the active catalyst reaching   35
twelve or more months, and at the same time sulphur compounds such as carbonyl sulfide (COS) being
hydrogenated into sulphydric acid, said acid being further removed on a zinc oxide bed;
   e)   passing a portion of the hydrogenated gas, stream G, effluent from hydrogenation reactor 5 from step
d) through a zinc oxide fixed bed reactor 6 in order to remove as zinc sulfide the sulphydric acid existing in

40 the refinery gas or produced in step d) followed by injection of the hydrogenated and sulphur free refinery   40
gas – stream K – in the water steam reformer;
   f)   returning a portion of the hydrogenated gas – stream H – effluent from the hydrogenation reactor 5 to
the heat exchanger 4 in order to cool said gas and give heat to the feed, followed by cooling said gas –
stream I – in the exchanger 7 with water, optionally boiler water, up to temperatures in the range of

45 170–140°C, preferably 150°C, separating in vessel 8 the liquid formed, followed by injection of said gas –   45
stream J – in the intermediate stage of the compressor 3.

2.   A PROCESS FOR THE SELF-HYDROGENATION of refinery gases from fluid catalutic cracking units
(FCC) and delayed coking, said gases containing from 6 to 15% olefins by volume according to claim 1,
characterized in that in the reaction step occurring in hydrogenation reactor 5, pressure is kept between 100

50 psi (7 kg/cm^2) and 713 psi (50 kg/cm^2), the temperature between 250 and 400°C, preferably 360°C, the hourly   50
space velocity is comprised between 700 h^{-1} and 2500 h^{-1}, preferably 1250 h^{-1}, such that, in the said
conditions of pressure, temperature and hourly space velocity the olefins are completely hydrogenated, the
carbon oxides methanation reactions present in the refinery gases, highly exothermic, are kept under
control, as well as the shift reaction of carbon monoxide to carbon dioxide.

55 3.   A PROCESS FOR THE SELF-HYDROGENATION of refinery gases from fluid catalytic cracking units   55
(FCC) and delayed coking, said gases containing from 6 to 15% olefins by volume according to claim 1,
characterized in that, in such process, is effected the hydrogenation of sulphur compounds such as carbonyl
sulfide, COS, said sulfide being further removed together with the sulphydric acid originally present in the
refinery gas, in a zinc oxide bed as zinc sulfide.

60 4.   A PROCESS FRO THE SELF-HYDROGENATION of refinery gases from fluid catalytic cracking units   60
(FCC) and delayed coking, said gases containing from 6 to 15% olefins by volume according to claim 1,
characterized in that the shift reaction of carbon monoxide present in the refinery gases produces carbon
dioxide through the reaction of said monoxide with the equilibrium water present in said gases.

5.   A PROCESS FOR THE SELF-HYDROGENATION of refinery gases from fluid catalytic cracking units

65 (FCC) and delayed coking, said gases containing from 6 to 15% olefins by volume, according to claim 1,   65

characterized in that due to the huge variations in the olefin level of the refinery gases, the hydrogenation reactor 5 is provided with adequate instrumentatation so as to avoid exceeding, at any moment, at any point of the bed, the temperature in which occurs great accelaration of the coke deposition reactions on the catalyst.

5 6.   A PROCESS FOR THE SELF-HYDROGENATION of refinery gases from fluid catalytic cracking units   5
(FCC) and delayed coking, said gases containing from 6 to 15% olefins by volume, according to claim 1,
characterized int that all the heat necessary to the hydrogenation reactions is obtained from said
hydrogenation reactions and all the required hydrogen is originally found in the refinery gases themselves,
thus not requiring additional injection of hydrogen from an external source.

10   7.   A PROCESS FOR THE SELF-HYDROGENATION of refinery gases from fluid catalytic cracking units   10
(FCC) and delayed coking, said gases containing from 6 to 15% olefins by volume, according to claim 1,
characterized in that is kept under control the rate of the coke deposition reactions on the catalyst.

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US-CL-CURRENT: 208/141

ABSTRACT:

CHG DATE=19990617 STATUS=O> A process for the self-hydrogenation of the olefins, present in refinery gases, at levels of 6-15% by volume or higher, whereby, after separating liquid from the refinery gases stream, a portion of said stream which makes up the feed of the ammonia unit, is admixed to saturated cooled recycle gas and compressed under controlled pressure and the mixture feed-recycle gas is hydrogenated in the fixed bed hydrogenation reactor, so as to reduce the olefin levels to less than 0.3% by weight, and at the same time COS is hydrogenated into H2S, a portion of the hydrogenated gas is carried to a zinc oxide reactor in order to remove H2S, the olefin-free and sulphur-free gas is injected in the steam reformer, another portion of the hydrogenated gas from the hydrogenation reactor is returned to a heat exchanger in order to give heat to the feed, said gas is cooled in another exchanger and the hydrogenated gas is injected in the compressor intermediate stage. □